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(71) Applicant
·Standard Telephones & Cables Public Limited Company,
(United Kingdom),
190 Strand, London WC2R 1DU

(72) Inventor
Philip William Black

(74) Agent and/or Address for Service
**S. R. Capsey,
Standard Telephones and Cables Public Limited Company,
Patents Department, Edinburgh Way, Harlow,
Essex CM20 2SH**

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(54) **Optical fibre manufacture**

(57) The ingress of hydrogen or moisture to an optical fibre, e.g. due to pressure when the fibre is in a cable on the seabed, has a deleterious effect on the fibre's optical performance. Hence it is desirable to provide the fibres in the cable each with a hydrogen barrier. This is done by the provision of an outer layer for the fibre which includes relatively large atoms, as described of boron or an inert gas such as argon.

The methods described are:

(a) entrapping large atoms or ions, e.g. argon atoms, in the interstices of the relatively open silica crystal lattice. This method can be used in association with the application to the fibre preform of a surface layer of TiO_2/SiO_2 by a vapour phase reaction,

(b) applying a surface layer of boron carbide to the surface of the preform/fibre during the drawing,

(c) applying an outer layer of a borosilicate glass to the fibre.

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SPECIFICATION

Optical fibre manufacture

5 This invention relates to the manufacture of optical
fibre preforms and optical fibres which may be ex-
posed to hydrogen, and to certain similar materials
such as those with hydroxyl ions.
    Under some circumstances hydrogen may be
10 generated within a capable or released from the
materials of the cable. The presence of this free
hydrogen can have a deleterious effect on the
transmission characteristics of the fibre and hence
of the cable. Hydrogen can diffuse into the struc-
15 ture of the fibre produced by standard methods,
and it has a number of effects. The major effect is
to produce a vibrational absorption spectrum
across a wide wavelength region. The detail of the
spectrum depends inter alia on the temperature of
20 the cable, and the partial pressure of hydrogen in
the vicinity of the fibre. Limited variations in the
height of the molecular hydrogen absorption peaks
can arise with changes in composition but the
main spectrum is unchanged. This particular mech-
25 anism is reversible.
    However, other effects of hydrogen on the trans-
mission performance are not reversible. In particu-
lar, permanent chemical changes and associated
losses have been reported in fibres containing
30 phosphorus. These changes are continuously de-
grading in the presence of hydrogen and increased
levels of loss at peaks associated with hydroxyl
ions bonded into the glass. This results, as seen by
the user of such a fibre in a cable, in a considera-
35 ble increase in the attenuation in the fibre.
    Thus the absorption of hydrogen into the fibre,
whether into its core or into its cladding, increases
the attenuation which the fibre presents to the light
which it is conveying. It should be noted that such
40 hydrogen absorption by the cladding is significant
in addition to absorption by the core. This is more
so in the case of single mode optical fibres than
for multi-mode fibres, since in the former case, as
was pointed out by C.P. Sandbank, "Fiber Optic
45 Communication: A Survey", Electrical Communica-
tions, Vol. 50, No. 1, 1975, pp 20-27, attenuation is
influenced to a much greater extent by the clad-
ding material than is the case for multi-mode
transmission.
50 The degradation of the characteristics of the fibre
due to the ingress of hydrogen is especially incon-
venient when the fibres involved are in a subma-
rine cable. In such use, it should be noted, the
ingress of hydrogen and its compounds is particu-
55 larly likely.
    An object of the invention is to manufacture op-
tical fibres in such ways as to provide barriers to
the ingress of hydrogen gas. Thus both the spec-
tral effects of molecular hydrogen and the perma-
60 nent loss changes due to chemically induced
changes related to hydrogen diffusion will be re-
duced to levels at which the optical performance of
the fibre when used in communications and other
systems is not impaired.
65 According to the invention there is provided a
method of inhibiting the diffusion of hydrogen and
similar gases into a silica optical fibre, which in-
cludes the provision of a layer on or within the
fibre which embodies or includes atoms or ions or
70 molecules of relatively large size compared with
the molecules of hydrogen, which relatively large
atoms or ions or molecules obstruct the diffusion
of hydrogen atoms into the transmitting region of
the fibre, and thus act as a hydrogen barrier.
75 In most cases the layer which includes the rela-
tively large obstructive atoms is the outer most
layer, but in some cases it may be a layer between
the cladding and the light-transmissive region.
    According to the invention, in a more specific
80 form, there is provided a method of inhibiting the
diffusion of hydrogen and similar gases into a sil-
ica optical fibre, which includes the introduction of
atoms of relatively large size compared with the
molecules of hydrogen, such as the atoms of inert
85 gas, into the pores or interstices of part of the non-
transmitting outer silica layer of the optical fibre.
    As will be seen from the subsequent description,
the preferred gas whose atoms are to be intro-
duced into the pores or interstices of the material
90 is argon. This is because argon, being an inert gas,
is essentially a monatomic gas, with relatively
large atoms. Further it has very little chemical
reactivity. The pores in the material referred to are
in fact the interstices in the glass structure, in the
95 case of silica between the silicon atoms and the
oxygen atoms.
    According to the invention, in another somewhat
more specific form, there is also provided a
method of inhibiting the diffusion of hydrogen into
100 a silica optical fibre, which includes applying to the
preform from which the fibre is to be drawn a
layer of a particulate soot by a vapour phase reac-
tion or by a similar method, consolidating the par-
ticulate layer to a clear glass by heating under
105 pressure in an atmosphere rich in an inert gas
such as neon or argon, thus causing atoms of the
inert gas to be entrapped in the pores or interstices
of the glass structure of the surface glass, and
thereafter drawing the preform to produce the
110 fibre, the atoms thus entrapped forming a hydro-
gen barrier to substantially prevent hydrogen diffu-
sion.
    According to another aspect of the invention,
there is further provided a method of inhibiting the
115 diffusion of hydrogen and similar gases into a sil-
ica optical fibre, which includes producing a barrier
layer of a borosilicate glass overlaying the optical
cladding of the fibre, the ratio of B_2O_3 to SiO_2 in the
borosilicate glass, being in the range of 1 to 6 in
120 mole per cent, the boron atoms providing the hy-
drogen barrier.
    Thus in this case the relatively large atoms
whose function is to obstruct the ingress of hydro-
gen are the boron atoms, which are large com-
125 pared with the hydrogen molecules whose passage
is to be obstructed.
    According to yet another aspect of the invention,
there is still further provided a method of inhibiting
the diffusion of hydrogen or similar gases into a
130 silica optical fibre, which includes producing a bar-

rier layer of boron carbide on the outer surface of
a silica fibre preform while that preform is being
drawn to produce the fibre, the boron atoms in the
layer thus produced providing the hydrogen bar-
5 rier.
    Here also the hydrogen molecule obstructive at-
oms are the atoms of boron.
    The first approach to the solution of the problem
of hydrogen diffusion to be considered herein de-
10 pends on the fact that with many glasses such as
silica glass, the atomic structure is relatively open
so that small atoms such as hydrogen atoms can
readily pass through the material to reach the im-
portant core and optical cladding regions of the
15 fibre. They may even, at least temporarily, take up
residence in the interstices of the lattices. Such dif-
fusion of hydrogen atoms into and through the
structures, in this case of the silicon and oxygen
atoms, causes the degradation of performance re-
20 ferred to above.
    This objectionable diffusion is prevented by in-
troducing relatively large atoms, ions or even mol-
ecules into or onto the outer region of the glass
fibre. This is effected in this first approach by the
25 creation of a gas barrier at the glass surface, i.e.
the surface of the fibre preform, or of the fibre it-
self, either after or during drawing.
    In one implementation of this approach, a pre-
form is coated on its outer surface with a layer of a
30 particulate, soot-like, silica by a vapour phase reac-
tion. The soot is then consolidated to a clear glass
by heating in an atmosphere which is rich in ar-
gon, which is chosen because it is an inert gas
whose atoms are relatively large, but not so large
35 as to cause stress in the surface of the glass. An
example of such an atmosphere is a helium-oxy-
gen-chlorine-argon mixture. The presence of chlor-
ine is intended to prevent hydroxyl (-OH)
formation, but is not essential provided the layer
40 under consideration is relatively remote from the
transmitting region. The other gases act in the
main as carriers for the gas whose atoms are to be
"stuffed" into the pores. A pressure higher than
that normally used for the gaseous atmosphere at
45 this stage of manufacture, e.g. two or three times
as great, is used.
    As a result of the above method, the glass forms
with argon atoms entrapped in the pores of the
surface glass. It will be appreciated that the time
50 needed to complete the consolidation of the soot-
like material into glass may be, and in fact usually
is, lengthened due to the presence of the argon.
When the outer glass layer has been thus pro-
duced, the thus-cladded preform can be drawn to
55 fibre in the normal manner. The closer-packed
atomic structure of the sintered glass retains the
atoms of the inert gas both in the preform and in
the fibre which results from the drawing operation.
    In another version of the above method, the sur-
60 face layer of the fibre is a titania/silica, TiO_2/SiO_2
layer which overlies the cladding layer of the fibre.
Such a layer also tends to provide a barrier to the
ingress of hydrogen and other offensive gases. The
layer is applied to the outer surface of the optical
65 fibre preform by a vapour phase reaction before

the drawing of the fibre. This layer is so applied as
to give the final fibre a layer of TiO_2/SiO_2 whose
thickness is in the range of 5 to 20 microns. Such a
layer, especially in the lower portion of its thick-
70 ness range has the additional merit that it is resist-
ant to strains due to compression. That is, it forms
a compressive surface layer in the final fibre,
which provides resistance to external strains. The
deposition of the TiO_2/SiO_2 layer is effected with
75 the deposition region containing the inert gas,
preferably argon, under pressure, as indicated
above. In this case the atoms of the inert gas enter
the interstices or pores of the silica/titania struc-
ture.
80   As in the case in which the fibre has an outer
layer of pure silica, the titania/silica layer is initially
in a particulate, soot-like form and is converted to
a glass by the application of heat prior to drawing.
As already indicated, such a titania/silica layer pro-
85 vides the finished fibre with an outer layer which
contributes to the hydrogen barrier action due to
the fact that its atoms are large compared with the
molecules of hydrogen. The layer also serves to
support the "stuffed" atoms. It also provides a
90 compressive surface coating which improves the
resistance of the fibre to fatigue.
    At this point it is worth referring to British Patent
Specification No. 2032910B (ISEC; K.C. Kao et al
20-7). In the arrangements described therein, an
95 optical fibre has, over its cladding, a layer of mate-
rial with a lower thermal expansion coefficient than
the rest of the fibre. This has been found to in-
crease the mechanical strength of the fibre. Such
an arrangement can also have a layer of higher
100 thermal expansion material between the cladding
and the just-mentioned low expansion layer. These
layers can be of borosilicate with an outer silica
layer or soda lime with an outer borosilicate layer.
    This Patent Specification mentions that the outer
105 layer referred to above excludes unwanted con-
taminants during manufacture, and among the
contaminates mentioned are hydrogen and hy-
droxyl compounds. However, although hydrogen
and hydroxyl exclusion is thus referred to, its sig-
110 nificance in its context is in the requirement to
avoid difficulties which could arise during the va-
pour phase reaction. What we have appreciated,
which is by no means apparent from the above-
mentioned Patent Specification, is that a borosili-
115 cate outer layer is also useful, if suitably applied,
for use as a hydrogen barrier during the life of a
cable which includes the fibre.
    The borosilicate layers used in the present ar-
rangements have relatively high boron content;
120 thus we have appreciated that a borosilicate layer
with a suitably high boron content is useful to pre-
vent hydrogen diffusion through the glass matrix.
This is because the presence of the boron atoms in
a silica glass reduces the pore size for hydrogen
125 migration, and thus provides a barrier against gas
diffusion. Here also a significant point is that the
boron atoms are significantly larger than hydrogen
molecules.
    Thus it will be seen that the borosilicate tech-
130 nique referred to herein, where the amount of bo-

ron present is relatively high, is in effect another
aspect of the "atom stuffing" technique described
above, since in both cases the hydrogen's move-
ment is obstructed by atoms which are relatively
5 large compared to hydrogen molecules.
   We will now describe two methods of providing
a borosilicate hydrogen barrier, in both of which
the ratio of B_2O_3 to SiO_2 is in the range of 1 to 6 in
mole per cent. The higher ratios of B_2O_3 to SiO_2 are
10 the preferred ones.
   In the first of these two methods internal vapour
phase diffusion is used, a boron-oxide rich silica
glass layer being deposited on the inner wall of a
silica substrate tube prior to the deposition of the
15 optical cladding and core compositions. Thus there
are three stages of deposition, (i) the borosilicate
layer in which the proportions of boron and silicon
in the vapour are appropriate to the desired rela-
tively high boron content of the outer layer, (ii) the
20 cladding layer and (iii) the core layer. The latter
two layers are deposited in a manner by now well
established in optical fibre technology. The first
layer is deposited, as indicated, using vapours with
the appropriate boron percentage and with suitable
25 carrier gases. This deposition can also to a large
extent follow established technology.
   After the depositions described above, the tube
is collapsed to form a solid preform, which is sub-
sequently drawn to produce the fibre. The fibre
30 thus consists of a light-transmitting core overlayed
by a lower refractive index cladding which in its
turn is overlayed by the boron-oxide rich layer. The
layer thus produced is a physical barrier, which is
analogous to the physical barrier provided by the
35 "stuffed" atoms of the other method described
above. It is outside the region of optical field pene-
tration in normal operating conditions, which pro-
vides a distinction between the otherwise-related
borosilicate and "atom stuffing" methods.
40   In the method just described, a pure silica layer
may, if desired, be deposited between the borosili-
cate glass and the deposited material of the clad-
ding to minimise diffusion of boron into the
cladding if this is considered necessary or desira-
45 ble. Such a layer when used has a thickness in the
range of 5 to 10 microns.
   The second method of producing the borosilicate
rich outer layer uses external vapour phase deposi-
tion on the surface of a preform rod. Here the bo-
50 rosilicate (or possibly borosilicide) glass is formed
as a particulate or soot-like layer, and is subse-
quently fused to a solid glass layer. A surface layer
of pure silica grown in a similar way, or by plasma
deposition as a glass, may be applied over the bar-
55 rier layer to maintain the mechanical strength and
durability of the fibre.
   Another approach to the use of relatively large
atoms as a hydrogen barrier is to apply a layer of
boron carbide to the surface of the silica fibre
60 while drawing the fibre from the preform. It will be
seen that this approach is closely related to the
methods using borosilicate glass. The boron car-
bide is applied to the fibre by a vapour phase reac-
tion at a temperature which is relatively low
65 compared with the temperature used for the other

depositions. The preform used is made in conven-
tional manner, and as usual includes a doped silica
core with a cladding of a lower refractive index ov-
erlaying it. This approach, like the other ap-
70 proaches to the provisions of a hydrogen barrier
described herein, is applicable to the production of
mono-mode, single mode graded index, and
stepped index fibres.
   The boron carbide layer, the thickness of which
75 is in the range of 5-15 microns in the completed
fibre, provides a hermetic seal against the ingress
of gases including hydrogen, and also against
moisture, which latter contains hydrogen. The
presence of such a seal improves the fibre's relia-
80 bility and prevents degradation of the fibre's opti-
cal performance in the presence of hydrogen and
other gases.
   It will be appreciated that the barrier layer ap-
plied to the fibre to resist the ingress of hydrogen
85 and other unwanted gases may have dopants for
other purposes, provided that they do not reduce
the efficiency of the barrier as an anti-diffusant.

CLAIMS

90   1. A method of inhibiting the diffusion of hy-
drogen and similar gases into a silica optical fibre,
which includes the provision of a layer on or
within the fibre which embodies or includes atoms
95 or ions or molecules of relatively large size com-
pared with the molecules of hydrogen, which rela-
tively large atoms or ions or molecules obstruct
the diffusion of hydrogen atoms into the transmit-
ting region of the fibre, and thus act as a hydrogen
100 barrier.
   2. A method as claimed in claim 1, and in
which said layer is formed by the application to the
fibre or its cladding of an outer layer of a boron
compound such as borosilicate having a relatively
105 high boron content or of boron carbide having a
relatively high boron content, the boron atoms
being the relatively large atoms referred to in claim
1.
   3. A method as claimed in claim 1 or 2, and in
110 which the large atoms or ions are provided by in-
troducing relatively large atoms, ions, or mole-
cules, e.g. inert gas atoms, into the pores or
interstices of the atomic lattice of the outer layer of
the fibre, the atoms thus introduced forming the
115 hydrogen barrier.
   4. A method of inhibiting the diffusion of hy-
drogen and similar gases into a silica optical fibre,
which includes the introduction of atoms of rela-
tively large size compared with the molecules of
120 hydrogen, such as the atoms of inert gas, into the
pores or interstices of part of the non-transmitting
outer silica layer of the optical fibre.
   5. A method as claimed in claim 4, in which the
atoms to be introduced into said pores or inters-
125 tices are atoms of argon, and in which said intro-
duction is effected by the application of a gas
stream under high temperature and pressure, the
stream being a helium-oxygen-chlorine-argon mix-
ture.
130   6. A method of inhibiting the diffusion of hy-

drogen into a silica optical fibre, which includes applying to the preform from which the fibre is to be drawn a layer of a particulate soot by a vapour phase reaction or by a similar method, consolidat-
5 ing the particulate layer to a clear glass by heating under pressure in an atmosphere rich in an inert gas such as neon or argon, thus causing atoms of the inert gas to be entrapped in the pores or interstices of the glass structure of the surface glass,
10 and thereafter drawing the preform to produce the fibre, the atoms thus entrapped forming a hydrogen barrier to substantially prevent hydrogen diffusion.

7. A method as claimed in claim 6, and in
15 which the particulate soot is pure silica.

8. A method as claimed in claim 6, and in which the particulate soot is a titania/silica mixture.

9. A method of inhibiting the diffusion of hydrogen and similar gases into a silica optical fibre,
20 which includes producing a barrier layer of a borosilicate glass overlaying the optical cladding of the fibre, the ratio of B_2O_3 to SiO_2 in the borosilicate glass, being in the range of 1 to 6 in mole per cent, the boron atoms providing the hydrogen barrier.

25 10. A method as claimed in claim 9, in which internal vapour phase reaction is used to initially produce the layer of a boron-oxide rich glass layer on the inner wall of a silica substrate tube, whereafter the cladding and the core are produced, the
30 preform made therefrom being drawn to produce the fibre.

11. A method as claimed in claim 10, and in which a layer of pure silica glass is deposited between the borosilicate layer and the cladding.

35 12. A method as claimed in claim 9, and in which the borosilicate layer is deposited on the outer surface of an optical fibre preform as a particulate layer and is thereafter fused to a solid glass layer, the preform thus produced being
40 drawn to produce the fibre.

13. A method of inhibiting the diffusion of hydrogen and similar gases into a silica optical fibre, which includes producing a barrier layer of a borosilicide glass overlaying the optical cladding of the
45 fibre, the boron atoms in the borosilicide layer providing the hydrogen barrier.

14. A method as claimed in claim 13, and in which the borosilicide layer is deposited on the outer surface of an optical fibre preform as a par-
50 ticulate layer and is thereafter fused to a solid glass layer, the preform thus produced being drawn to produce the fibre.

15. A method as claimed in claim 9, 10, 11 or 12, and in which a surface layer of pure silica is
55 applied over the barrier layer.

16. A method of inhibiting the diffusion of hydrogen or similar gases into a silica optical fibre, which includes producing a barrier layer of boron carbide on the outer surface of a silica fibre pre-
60 form while that preform is being drawn to produce the fibre, the boron atoms of the layer thus produced providing the hydrogen barrier.

17. A method as claimed in claim 16, and in which the boron carbide is applied by a vapour
65 phase reaction at a temperature which is relatively

low compared with the temperatures used for the deposition of the cladding and core materials.

18. A method of inhibiting the diffusion of hydrogen or similar gases to a silica optical fibre,
70 substantially as described herein.

19. A silica optical fibre to which the method of any one of claims 1 to 18 has been applied.

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